Note on Opalescence in Fluids near the Critical Temperature.

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The phenomenon of opalescence at and near the critical temperature has been observed by Travers and Usher* under exceptionally favourable conditions, owing to the great width (8 to 10 mm. internal diameter) of the tubes they employed. The opalescence is, however, distinctly visible, and can be studied in much narrower tubes, such as those (0·15 mm. internal diameter) used in my own investigations.

The experiments of Travers and Usher were carried out, for the most part, in such a manner that the total volume of the substance investigated remained constant, while the temperature rose very slowly. In my experiments, on the other hand, the substance was kept at its critical temperature,† and the volume was altered (usually diminished) by equal stages. The opalescence was always seen, but notes of its position and character were only made with a few substances—isopentane and normal pentane, hexane, and octane.

My observations—mostly unpublished—may be regarded as supplementing and, so far as a comparison is possible, confirming those of Travers and Usher, and the following generalisations may be deduced from them:—

1. When observations are made at the critical temperature (Cagniard-Latour temperature) at a series of diminishing volumes, no opalescence is visible so long as the volume exceeds a definite limit. When this limiting volume is passed, a slight opalescence appears at the bottom of the tube, that is to say, just over the mercury; at still smaller volumes the opalescence or mist becomes denser and extends further up the tube. Near the critical volume the mist is very dense, especially near the middle; it may extend all through the tube, or the tube may appear clear either at the top or both at top and bottom. When the volume is further reduced, the mist disappears below, but becomes dense above, and on further compression the clear part extends upwards and the remaining mist at the top becomes less dense and finally disappears at a definite volume.

When observations at the critical temperature are made at a series of increasing volumes, there is a tendency for the mist to be lower down in the tube than when they are made during compression. This tendency may

* *Supra*, p. 249.

† In the case of normal pentane the "Cagniard-Latour temperature" and the "critical temperature" were found to be identical or at least indistinguishable ('Trans. Chem. Soc.,' vol. 71, p. 446, 1897).

probably be explained by the fact that each expansion causes a temporary slight fall below the critical temperature and, consequently, a very slight condensation from the critical to the liquid state (in three cases it was noted that the meniscus was actually seen for a moment). Some little time would be required for equilibrium to be re-established after such a disturbance of the density, and it may be that the time actually allowed—one or two minutes at most—was insufficient. On the other hand, during each compression, there is a very slight rise of temperature, but this does not cause any change of state or disturbance of density.

2. When observations are made at a temperature slightly higher than the critical temperature, the mist is not only much less dense, but the range of volume over which it is visible is more restricted.

3. The limits of volume between which mist is visible at the critical temperature seem to be nearly the same for the four paraffins examined (about 1·17 or 1·18 to about 0·87 or 0·88, taking the critical volume as unity in each case).

One conclusion drawn by Travers and Usher from their experiments is that "the opalescence is confined to that phase which is decreasing in volume through movement of the dividing surface, or, at least, is most intense in that phase." It happens, however, that in their experiments, whenever the liquid phase was small at first, it diminished, and when large at first, it increased; and it may be doubted whether the above relation would be found to hold good for a phase which was large but decreasing in volume, for example, under the following conditions: (*a*) constant volume and slowly falling temperature; (*b*) constant temperature and the total volume either large but decreasing, or small but increasing.

It seems probable from my experiments that the position of maximum opalescence really depends on the mean specific volume of the substance, being near the bottom when the volume is large, near the top when small, and near the middle at intermediate volumes.

This question, although it does not affect the main conclusions arrived at by Travers and Usher, seems to be of sufficient interest to repay further investigation.